Growth of high-quality $Ga_xIn_{1-x}As_yP_{1-y}$ by chemical beam epitaxy

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$Ga_xIn_{1-x}As_yP_{1-y}$ epilayers closely lattice matched, $\Delta a/a \lesssim 5\times10^{-4}$, have been reproducibly grown over the whole range of composition ($y = 2.2x$, $1 > y > 0$) by chemical beam epitaxy. The relative sticking coefficient (or equivalently the incorporation efficiency into the solid) of arsenic to phosphorus, i.e., S_{As}/S_P was between 1.5 and 3 depending on the material composition. Such values indicate a very efficient incorporation of phosphorus in this process. Very intense efficient luminescence peaks due to excitonic transitions with linewidths full width at half-maximum as narrow as 3 meV were obtained. Such a linewidth corresponds closely to the intrinsic linewidth due to alloy broadening in GaInAsP alloys. Furthermore, the photoluminescence spectra revealed that the donor-to-acceptor pair recombination was nearly absent. Hall measurements on $Ga_xIn_{1-x}As_yP_{1-y}$ epilayers lattice matched into InP at 300 and 77 K yielded electron mobility values that agreed closely with theoretical values calculated by using the one-phonon model and the electronegativity difference as the alloy scattering potential for layers with doping levels between 1×10^{15} cm^{-3} and 1×10^{16} cm^{-3}. The 77 K electron mobilities ranged from 2.2×10^4 to 6.7×10^4 $cm^2/V\,s$ depending on the quaternary composition.

Even though $Ga_xIn_{1-x}As_yP_{1-y}$ quaternaries have been extensively grown by liquid phase epitaxy (LPE),[1] metalorganic chemical vapor deposition (MOCVD),[2,3] and hydride vapor phase epitaxy (VPE),[4] and to a lesser extent by solid source[5] and gas source molecular beam epitaxy (GSMBE)[6,7] for optoelectronic device applications, relatively little has been published on the characterization of these quaternary epilayers. Recently, chemical beam epitaxy (CBE) has been employed to produce high-quality GaAs, InP, and $Ga_{0.47}In_{0.53}As$ epilayers,[8–13] GaAs/AlGaAs and $Ga_{0.47}In_{0.53}As$/InP quantum wells,[14–16] and electronic and photonic devices.[17–20] In this letter, we report the growth and material characterization of quaternary alloys $Ga_xIn_{1-x}As_yP_{1-y}$ ($y\approx2.2x, 0<y<1$) lattice matched to InP by using CBE.

A gas handling system similar to that employed in Ref. 8 with the addition of a vent-line and input-pressure control for each gas channel was used. Precision electronic mass flow controllers were used for controlling the flow rates of the various gases admitted into the growth chamber. Separate gas inlets were used for group III organometallics and group V hydrides. A low-pressure arsine (AsH_3) and phosphine (PH_3) cracker with a reduced input pressure of ~50–200 Torr maintained on the high-pressure side of the electronic mass flow controllers was used. This presents less safety hazard as all the toxic gas pressure inside the manifold outside the gas storage cabinet is less than ~200 Torr. The cracking temperature was ~920 °C. Complete decomposition of AsH_3 and PH_3 into arsenic, phosphorus, and hydrogen was routinely achieved as observed by the absence of arsine and phosphine peaks inside the growth chamber with an *in situ* residue gas analyzer. Triethylgallium (TEGa) maintained at 30 °C and trimethylindium (TMIn) at 37 °C were used with H_2 as the carrier gas. The TEGa and TMIn flows were combined into a single beam with the effusion cell at ~50 °C. Iron-doped (100) InP substrates were used. The typical growth rate for GaInAsP quaternaries was ~3.8 μm/h. The growth temperature was ~555 °C.

The quaternary epilayers, typically 1–1.5 μm thick, were characterized by using double-crystal x-ray diffraction, photoluminescence spectroscopy, and Hall mobility measurements at 300 and 77 K. Figure 1 shows three ~1.5-μm band-gap GaInAsP epilayers with lattice mismatch $\Delta a/a \sim 1.3\times10^{-3}$, 6.5×10^{-4}, and exact matching. It is seen that in all cases the linewidths of the quaternaries are similar to that of the InP substrate indicating the high degree of crystalline integrity and composition uniformity achieved. Such linewidths and lattice matching were also obtained for epilayers from the entire range of $Ga_xIn_{1-x}As_yP_{1-y}$ ($y\approx2.2x, 0<y<1$) composition. The results of these studies are summarized in Fig. 2. Here, the relative flow rates of diluted TEGa (15% in H_2) to TMIn (10% in H_2), and pure PH_3 to AsH_3 necessary for maintaining close lattice matching, i.e., $\Delta a/a \lesssim 5\times10^{-4}$, to InP are plotted as a function of the band-gap wavelengths (measured from the room-temperature photoluminescence peaks) of the quaternaries. The absence of scattering in the present data indicates the excellent flow control and reproducibility achieved. The shape of the curves depended on the linearity of the mass flow controllers employed. However, for the same set of mass flow controllers used, a great degree of reproducibility was maintained over more than a year with only minor adjustments.

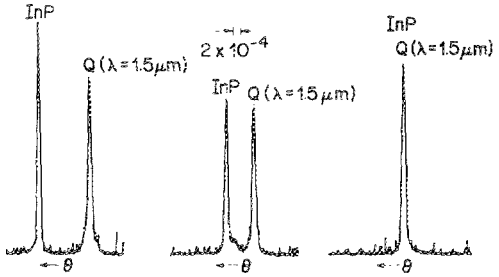

FIG. 1. Double-crystal x-ray diffraction spectra for three ~1.5-μm band-gap GaInAsP epilayers (~1.0 μm thick) having different amounts of lattice mismatch.

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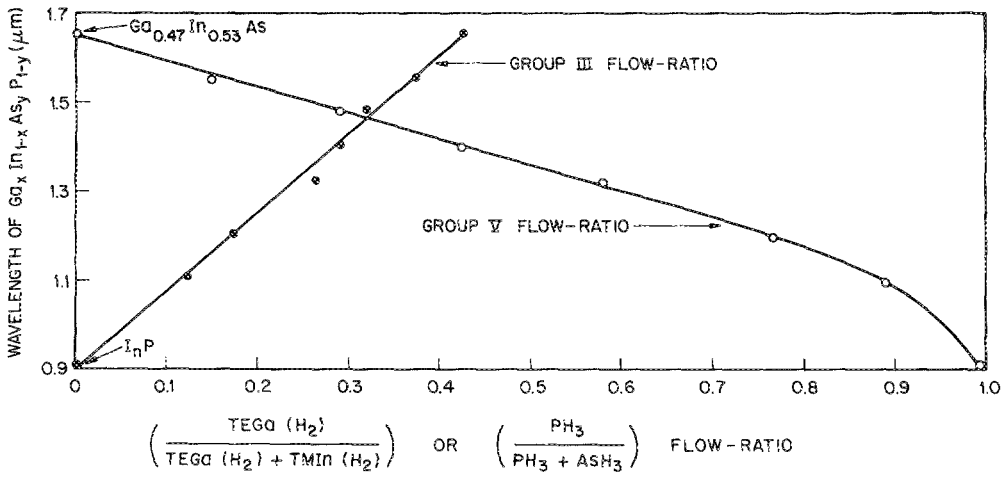

FIG. 2. Relative flow rates of diluted TEGa (15% in H_2) to TMIn (10% in H_2), and pure PH_3 to AsH_3 necessary for maintaining close lattice matching, i.e., $\Delta a/a \lesssim 5\times10^{-4}$, to InP were plotted as a function of the band-gap wavelengths measured from the 300 K photoluminescence peaks.

Though both AsH_3 and PH_3 are completely decomposed by the high-temperature cracker, the exact ratios of arsenic and phosphorus monomers, dimers, and tetramers resulted are not known. Different species are expected to have different incorporation rates. To maintain a constant reproducible ratio, the cracker temperature was maintained the same in every run at 920 °C even though we found it appeared not to be critical as long as it was above ~900 °C.

An estimate can be made of the relative sticking coefficient of arsenic to phosphorus, i.e., S_{As}/S_P, in the present techinque. For a growth temperature of 555 °C, the 1.55-μm composition value ($y\approx0.9$) was obtained with a phosphorus to arsenic beam flux ratio of 0.18 corresponding to a $S_{As}/S_P = 1.6$. For the 1.3-μm composition value ($y\approx0.66$), the estimated S_{As}/S_P was 2.7. These values indicate that the incorporation of phosphorus into the solid film is very efficient in our present technique. It is important to note that these values are significantly different from those obtained in GSMBE.[6,7] The difference may arise from the difference in surface chemistries occurring on the heated substrate surface. In CBE it involves surface pyrolysis of group III organometallics, while in GSMBE it involves atomic group III elements.

The 300 and 4 K photoluminesence spectra for quaternaries having room-temperature band-gap wavelengths at 1.1, 1.2, 1.3, 1.5, and 1.55 μm are shown in Figs. 3(a) and 3(b), respectively. Very intense efficient luminescence peaks due to excitonic transitions with linewidths (FWHM) typically 3–5 meV for all quaternaries were obtained at 4 K as shown in Fig. 3(b).

Photoluminescence linewidths and *alloy* compound semiconductors are broadened as compared to linewidths in binary semiconductors. Alloy broadening of photoluminescence spectra is due to a spatial fluctuation of the band-gap energy due to random anion or cation distributions. In quaternary alloys such as GaInAsP line broadening is due to both statistical anion *and* cation distribution. The photoluminescence linewidth for $Ga_{47} In_{53} As$ has been determined theoretically[21] to be 1.6 meV. In quaternaries, linewidths are roughly larger by a factor $\sqrt{2}$ as compared to ternaries. Thus linewidths of 2–3 meV are expected for quaternaries with random anion and cation distribution and low impurity concentration ($N_D + N_A \lesssim 10^{15}$ cm^{-3}).

The measured linewidths of 3–5 meV shown in Fig. 3 closely correspond to the theoretically calculated values for GaInAsP quaternaries. These values are about twice as large as those for CBE-grown $Ga_{0.47} In_{0.53} As$[12] but significantly narrower than those in Ref. 7. The photoluminescence spectra also show no indication of donor-to-acceptor pair recombinations.[7] This indicates that the quaternaries are of high purity. The large-area material composition uniformity is demonstrated by the photoluminescence spectra taken at five different locations on a 2.5×2.5 cm epilayer (limited by the size of the substrate holder) shown in Fig. 3(a). For comparison in linewidth, the 300 K spectrum from the binary InP is also shown in Fig. 3(a).

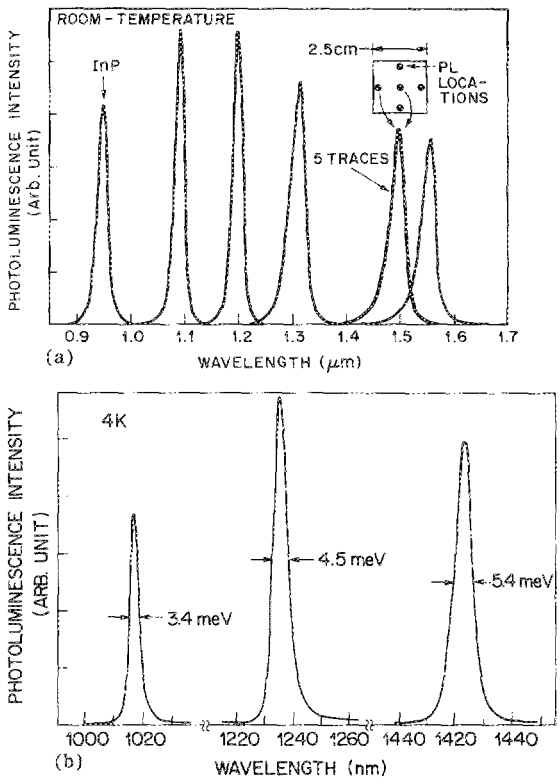

FIG. 3. 300 and 4 K photoluminescence spectra for GaInAsP quaternaries having 300 K band-gap wavelengths at ~1.1, 1.2, 1.3, 1.5, and 1.55 μm are shown in (a) and (b), respectively. The inset in (a) shows the large-area material composition uniformity. The spectrum for InP is shown for linewidth comparison.

Residual doping levels and electron mobilities were measured by Hall effect at 300 and 77 K on 1.0–1.5 μm thick epilayers. On the whole range of composition, $Ga_xIn_{1-x}As_yP_{1-y}$ ($y \approx 2.2x, 1 \geqslant y \geqslant 0$), the material is n type. These results are summarized in Fig. 4. The curves in this figure are calculated electron Hall mobilities in $Ga_xIn_{1-x}As_yP_{1-y}$ for $1 \geqslant y \geqslant 0$ by Takeda[22] using the one-LO-phonon model and the Philips' electronegativity difference as the alloy scattering potential. The upper group is for Hall mobility at 77 K, and the lower group is at 300 K. Full curves are calculated for a carrier compensation ratio = 1, and dashed curves for a carrier compensation ratio = 2. In both cases, electron concentrations of 1×10^{15} and 1×10^{16} cm^{-3} were calculated. It is seen that the present CBE results lie well within these curves for all compositions at both 300 and 77 K. Mobility values of 1.06×10^4 $cm^2/V\,s$ at 300 K and 6.5×10^4 $cm^2/V\,s$ at 77 K were achieved for ($y = 0.9$, $\lambda \approx 1.55\,\mu m$) quaternary epilayers with residual doping level of 2×10^{15} cm^{-3}. For comparison, some mobility results for LPE-[23] and GSMBE-grown[7] quaternaries are also shown in the same figure. In general, they are lower except for the ultrapure LPE-grown InP. The arrow bars at InP and $Ga_{0.47}In_{0.53}As$ indicate the range of 77 K mobilities obtained by LPE-grown epilayers.

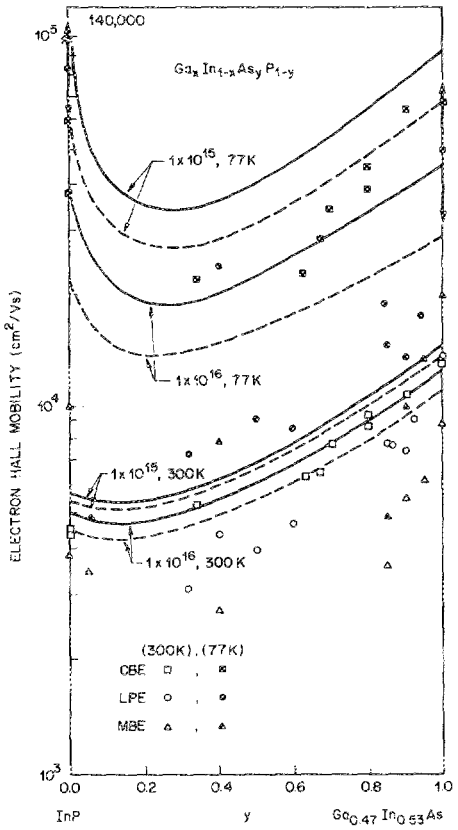

FIG. 4. Residual doping levels and electron mobilities measured by Hall effect at 300 and 77 K on 1–1.5 μm thick $Ga_xIn_{1-x}As_yP_{1-y}$ ($y \approx 2.2x, 1 \geqslant y \geqslant 0$) epilayers were plotted as a function of y. The curves are calculated electron mobilities in $Ga_xIn_{1-x}As_yP_{1-y}$ for $1 \geqslant y \geqslant 0$ by Takeda,[22] using the one-LO-phonon and the Phillips' electronegativity difference as the alloy scattering potential. The upper group is for Hall mobility at 77 K, and the lower group is at 300 K. Full curves are for Hall mobility with carrier compensation 1, and dashed curves for carrier compensation 2. In both cases, the electron concentrations of 1×10^{15} and 1×10^{16} cm^{-3} were calculated. For comparison, some mobilities for LPE-grown[22] and GSMBE-grown[7] quaternaries were also shown.

In summary, uniform large-area 11.5 cm^2 (limited by substrate holder) $Ga_xIn_{1-x}As_yP_{1-y}$ epilayers closely lattice matched, $\Delta a/a \lesssim 5\times10^{-4}$, have been reproducibly grown over the whole range of composition ($y = 2.2x$, $1 > y > 0$) by CBE. The relative sticking coefficient or equivalently the incorporation efficiency for arsenic to phosphorus, i.e., S_{As}/S_P, was found to lie between 1.5 and 3 depending on the material composition. Such values indicated a very efficient incorporation of phosphorus in this process. Very intense efficient luminescence peaks due to excitonic transitions with linewidths (FWHM) as narrow as 3 meV were obtained. Such linewidths closely correspond to the intrinsic linewidth due to alloy broadening in GaInAsP alloys. Furthermore, the photoluminescence spectra revealed that the donor-to-acceptor pair recombination was nearly absent. Hall measurements on $Ga_xIn_{1-x}As_yP_{1-y}$ epilayers lattice matched to InP at 300 and 77 K yielded electron mobility values that agreed closely with theoretical values calculated by Takeda[22] using the one-LO-phonon model and the Phillips' electronegativity difference as the alloy scattering potential for layers with residual doping levels between 1×10^{15} and 1×10^{16} cm^{-3}. The 77 K electron mobilities ranged from 2.2×10^4 to 6.7×10^4 $cm^2/V\,s$ depending on the quaternary composition.

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